

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : B41M 5/38 <i>file copy</i>	A1	(11) International Publication Number: WO 95/13195 (43) International Publication Date: 18 May 1995 (18.05.95)
(21) International Application Number: PCT/US94/11345 (22) International Filing Date: 6 October 1994 (06.10.94)	(81) Designated States: CA, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(30) Priority Data: 08/149,285 9 November 1993 (09.11.93) US	Published With international search report.	
(71) Applicant: MARKEM CORPORATION [US/US]; 150 Congress Street, Keene, NH 03431 (US). (72) Inventors: MENEGHINI, Frank, A.; 205 Chapman Road, Keene, NH 03431 (US). DEEKEN, John, S.; HCR Box 350, Sullivan, NH 03445 (US). DRAKE, John, J.; 20 Robbins Road, Keene, NH 03431 (US). (74) Agent: FEIGENBAUM, David, L.; Fish & Richardson, 225 Franklin Street, Boston, MA 02110-2804 (US).	<i># US. PN 5,757,313</i> Similar to which is a CIP of this references priority document.	

(S4) Title: TRANSFER PRINTING MEDIUM

## (57) Abstract

A transfer printing medium that includes a carrier to which is applied a curable laser-transferrable ink having one or more layers. The transfer medium is capable of converting laser energy to heat. The ink includes: (a) at least one colorant; (b) at least one polymerization initiator; and (c) at least one curable prepolymer.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

TRANSFER PRINTING MEDIUM

Background of the Invention

This invention relates to laser-induced transfer  
5 printing.

In laser-induced transfer printing, irradiation of  
an ink-bearing carrier with laser light causes the ink to  
transfer from the carrier to a surface, e.g., the surface  
of a microelectronic device, audio cassette, computer  
10 diskette, or syringe body. By manipulating the scanning  
parameters of the laser beam, the ink can be deposited in  
a programmed pattern.

Summary of the Invention

In a first aspect, the invention features a  
15 transfer printing medium that includes a carrier to which  
is applied a curable laser-transferrable ink having one  
or more layers. The transfer medium is capable of  
converting laser energy to heat. The ink includes (a) at  
least one colorant; (b) at least one polymerization  
20 initiator; and (c) at least one curable prepolymer. By  
"colorant" it is meant any additive that imparts color to  
the ink, including the colors white and black. Colorants  
include both dyes and pigments, as well as metallized  
coatings. By "prepolymer" it is meant any species  
25 capable of being polymerized following either thermal or  
photochemical initiation to form a polymer.

In preferred embodiments, the ink transfers to a  
surface of interest and cures in one step upon  
application of laser energy. In one preferred  
30 embodiment, at least one of the polymerization initiators  
is a thermal polymerization initiator and at least one of  
the prepolymers is thermally curable. In another  
preferred embodiment, at least one of the polymerization  
initiators is a photoinitiator and at least one of the  
35 prepolymers is photochemically curable.

One example of a preferred prepolymer is an epoxy-functionalized prepolymer. A second example is an epoxy-functionalized prepolymer combined with a vinyl ether-functionalized prepolymer. A third example is an epoxy-functionalized prepolymer combined with an acrylate-functionalized prepolymer. A fourth example includes the acrylate-functionalized prepolymers themselves. A fifth example is a blocked isocyanate-functionalized prepolymer and a sixth example is a blend of a vinyl ether-functionalized prepolymer and a maleate- or maleimide-functionalized prepolymer.

At least one of the ink layers may be a curable size coat that includes a polymerization initiator and a curable prepolymer. The size coat is used in combination with a color coat layer. In one preferred embodiment, the color coat is non-curable and includes a colorant and a thermoplastic film-forming resin. In another preferred embodiment, the color coat is curable and includes a colorant, a polymerization initiator, and a curable prepolymer. In the case of curable color coats used with curable size coats, the polymerization initiators and prepolymers found in the respective layers may be the same as, or different from, each other.

In a second aspect, the invention features a laser-induced transfer printing method using the above-described transfer printing medium. The method includes the steps of irradiating the particular transfer printing medium with laser light of a predetermined wavelength to transfer the ink from the carrier to a surface of interest, and curing the ink to adhere the ink to the surface of interest. The transfer and cure of the ink may be effected in a single step through irradiation with said laser light. Cure may also be effected in a separate step subsequent to transfer.

The invention provides transfer printing media featuring curable inks that adhere well to the surface on which they are deposited following laser irradiation. The inks transfer cleanly from the supporting carrier and 5 cure rapidly; in some cases, transfer and cure are effected in a single step. It is not necessary to add a separate self-oxidizing material such as nitrocellulose in order to effect transfer. In addition, the ability to use non-curable layers (e.g., non-curable color coats) in 10 combination with curable layers (e.g., curable size coats) expands the types of materials that can be used for the inks, enabling the properties of the inks to be adjusted as needed for a particular application.

Other features and advantages of the invention 15 will be apparent from the following description of the preferred embodiments thereof, and from the claims.

Description of the Preferred Embodiments

The invention features a transfer printing medium capable of converting laser energy to heat in which a 20 curable laser-transferrable ink having one or more layers is deposited on a carrier. The carrier must have sufficiently low surface energy to permit transfer of the ink. It also must not melt or otherwise deform upon laser irradiation. Examples of suitable carriers include 25 flexible plastic films such as polyethylene, polypropylene, and polyester.

The transfer medium is capable of converting laser energy to heat to promote transfer of the ink from the carrier to the surface of interest. To this end, one or 30 more thermal convertors are incorporated into the carrier, the ink, or both. The thermal convertors may be separate additives or may be part of the prepolymer.

In the case of separately added convertors included in the ink, the amount of convertor ranges from 35 about 0.25 to about 30% by weight (based upon the total

s lids content of the ink). The particular convertor is selected based upon the particular laser energy used for irradiation. In the case of CO<sub>2</sub> lasers, the preferred convertors are carbon black, polyethylene glycol (e.g., 5 PEG 3000 commercially available from Union Carbide), talc (e.g., Nytal 400 commercially available from R.T. Vanderbilt), and PPZ, a phosphotriazine commercially available from Idemitsu Petrochemicals Co. Ltd; PPZ may also function as a prepolymer. In the case of Nd:YAG 10 lasers, the preferred convertors are IR99, IRA 980, and IR165, all of which are proprietary dyes commercially available from Glendale Protective Technologies, IR dye 14,617 (a proprietary dye commercially available from Eastman Kodak), and Projet 900NP (a proprietary dye 15 commercially available from ICI). In the case of diode lasers, the preferred convertors are IR dye 14,617 and IRA 980.

The inks may have one or more layers, with particular ingredients (e.g., prepolymer, polymerization 20 initiator, etc.) being present in any of the layers. One example of ink is a one layer ink (referred to here as a "one-pass" coating) having a curable color coat that includes, in a single layer, a curable prepolymer, a polymerization initiator, and a colorant. Another 25 example is a two layer ink (referred to here as a "two-pass" coating) having a color coat (which may be curable or non-curable) in combination with an overlying curable size coat that includes a curable prepolymer and a polymerization initiator.

Because the inks are curable, adhesion upon transfer to a surface of interest is improved. The advantage of the size coat (which is transferred with the color coat upon laser irradiation) is that adhesion is further enhanced, thereby making it possible to use even 35 a non-curable color coat.

The inks contain one or more curable prepolymers, with the total amount of curable prepolymer ranging from 25 to 95% by weight (based upon the total solids content of the ink). Curable prepolymers useful in the invention  
5 have two or more functional groups available for crosslinking (which occurs either simultaneously with transfer upon application of laser radiation or following laser irradiation in a separate thermal or photochemical cure step).

10 One class of suitable curable prepolymers includes epoxy-functionalized prepolymers such as bisphenol A diglycidyl ether (commercially available from Shell Oil under the designation Epon 1001) and epoxy-functionalized novolac resins (e.g., Epon 164 commercially available  
15 from Shell Oil). Lower molecular epoxides such as UVR6110 (a liquid diepoxide commercially available from Union Carbide) may be added as well.

A second class of suitable curable prepolymers includes these epoxy-functionalized prepolymers in  
20 combination with one or more vinyl ether-functionalized prepolymers which co-cure with the epoxy-functionalized prepolymers. Examples of suitable vinyl ether-functionalized prepolymers include bisphenol A-divinyl ether adduct; 2,4-toluene diisocyanate/hydroxybutyl vinyl  
25 ether adduct; cyclohexyl divinyl ether commercially available from GAF or ISI Products; vinyl ethyl ether, vinyl isobutyl ether, vinyl octadecyl ether, polyethylene glycol divinyl ether, polytetrahydrofuran/350/divinyl ether, and trimethylol propane trivinyl ether, all of  
30 which are commercially available from BASF; Rapi/cure divinyl ether/3, Rapi/cure cyclohexyl vinyl ether, Rapi/cure PEPC, and Rapi/cure hydroxy butyl vinyl ether, all of which are commercially available from ISP; and Vectomers 2010, 2031, 2032, 4010, 4020, and 4030, all of  
35 which are commercially available from Allied-Signal.

A third class of suitable curable prepolymers includes the above-described epoxy-functionalized prepolymers in combination with one or more acrylate-functionalized prepolymers. Examples of acrylate-functionalized prepolymers include RDX 29522 and Ebecryl 639 (both of which are commercially available from Radcure); Sartomer 351 (commercially available from Sartomer); and NR440 (commercially available from Zeneca Resins).

10 A fourth class of suitable curable prepolymers includes the acrylate-functionalized prepolymers themselves without the epoxy-functionalized prepolymers.

15 A fifth class of suitable curable prepolymers includes blocked isocyanate-functionalized prepolymers. Examples include B1299 (commercially available from Huls) and BL4165A (commercially available from Miles).

20 A sixth class of suitable curable prepolymers includes the above-described vinyl ether-functionalized prepolymers in combination with maleate- or maleimide-functionalized prepolymers. Examples of maleate-functionalized prepolymers include 89-8902 (commercially available from Cargil Products); and Astrocure 78HV and Astrocure 78LV (both of which are commercially available from Zircon). Examples of maleimide-functionalized

25 prepolymers include BMI/S/M/20/TDA (commercially available from Mitsui Toatsu Chemical, Inc.

30 One or more non-curable layers may be used in combination with one or more curable layers. For example, a non-curable color coat may be combined with an overlying curable size coat. Suitable non-curable resins are thermoplastic film-forming resins. Examples include acrylic resins such as Rhoplex B85 (an acrylic dispersion commercially available from Rohm & Haas) and Amsco 3011 (an acrylic dispersion available from Rohm & Haas);

35 urethane resins such as QW-16 (a urethane dispersion

useful as a film-former that is commercially available from K.J. Quinn); phenoxy resins such as PKHW 35 (commercially available from Union Carbide); and combinations thereof. The amount of non-curable 5 prepolymer in the ink ranges from about 15 to about 35% by weight (based upon the total solids content of the ink).

The inks also contain a polymerization initiator in an amount ranging from about 0.1 to 5% by weight 10 (based upon the total solids content of the ink). The initiator (which typically is a free radical or cationic initiator) may be a photochemical initiator or a thermal initiator; in some cases, the same initiator can act as both a thermal and a photochemical initiator. In the 15 case of multi-layer inks containing multiple curable layers, layers containing photochemical initiators may be combined with layers containing thermal initiators. In addition, some initiators may be used in conjunction with accelerators such as benzpinacole, copper II salts (e.g., 20 copper benzoate), and hexaphenylethane.

In the case of thermal initiators, the initiator must exhibit good stability at ambient temperature to prevent premature curing of the prepolymer. In addition, the initiation temperature must be within the range 25 achievable by laser irradiation. Examples of suitable thermal initiators for cationic initiation include aryl sulfonium salts (e.g., the salts described in WO90/11303, hereby incorporated by reference); aryl iodonium salts (e.g., UVE 9310 and U 479, both of which are commercially 30 available from General Electric); and ammonium salts (e.g., FC520, commercially available from 3M). Examples of suitable thermal initiators for free radical initiation include the class of compounds leading to peroxy radicals, e.g., hydroperoxides, peroxyesters, and 35 peroxyketals; representative compounds are commercially

available from Elf-Atochem. Also suitable for free radical initiation are azo polymerization initiators commercially available from Wako.

In the case of photochemical initiators, the 5 initiator must also exhibit good stability at ambient temperature to prevent premature curing of the prepolymer. In addition, it must exhibit absorption maxima in regions of the electromagnetic spectrum different from the regions in which the colorant exhibits 10 absorption maxima. Examples of suitable photochemical initiators for cationic initiation include aryl sulfonium salts (e.g., UVI 6974 commercially available from Union Carbide) and aryl iodonium salts (e.g., UVE 9310 and U 479, both of which are commercially available from 15 General Electric). Another example of a suitable initiator for cationic initiation is hydroxy naphthyl imide sulfonate ester. Examples of suitable photochemical initiators for free radical initiation include CPTX and ITX (both commercially available from 20 Ciba-Geigy), each of which is combined with methyl diethanolamine (commercially available from Aldrich Chemical Co.; lucerin TPO (commercially available from BASF) combined with methyl diethanolamine; Darcure 4265 (commercially available from Ciba Geigy), and Irgacure 25 369 combined with ITX.

The ink contains one or more colorants, which may be dyes, pigments, or metallized coatings (e.g., an aluminized coating). In the case of dyes and pigments, the colorant is present in an amount ranging from about 30 35 to 65% by weight (based upon the total solids content of the ink). The particular colorant is chosen based upon the color desired on the final printed surface. Examples of suitable colorants include pigments such as talc, TiO<sub>2</sub> (white), phthalogreen (GT-674-D), chrome green 35 oxide (6099), ultramarine blue (RS-9), black oxide (BK-

5099D), Kroma red (7097), and Novaperm yellow (HR-70), and dyes such as dynonicidine (2915) and Dianell orange, as well as the aforementioned metallized coatings.

In the case of inks containing photocurable 5 prepolymers, a sensitizer may be added in an amount ranging from about 0.5 to 8% by weight (based upon the total solids content of the ink) to extend the irradiating wavelength for photoinitiation into the visible region. Such sensitizers are useful, for 10 example, where the formulation contains large amounts of TiO<sub>2</sub> pigment which absorbs light below 400 nm and thus competes with the initiator. Examples of suitable sensitizers, all of which are commercially available from Aldrich Chemical Co., include perylene, rubrene, 15 phenothiazine, anthracene derivatives, and thioxanthones, as well as lucerin TPO (commercially available from BASF).

Other ingredients which may be added to the inks to improve the coatability, printability, print 20 performance, and durability of the inks include various surfactants, dispersing agents, and polymer dispersions. The amount of each ingredient is selected based upon the desired properties. Examples of suitable surfactants (which may be anionic, cationic, or nonionic) include 25 Triton X-100 (an aryl ethoxylate commercially available from Rohm & Haas) and FC 430 (a fluoroaliphatic polymeric ester available from 3M). Examples of suitable dispersing agents include polyacrylate salts such as Daxad 30, a 30% aqueous solution of polysodiumacrylate 30 commercially available from W.R. Grace. Examples of suitable dispersions include Shamrock 375 and Aquacer 355, both of which are polyethylene wax dispersions commercially available from Diamond Shamrock.

The transfer medium according to the invention is 35 prepared by combining the ink ingredients in an aqueous

or organic solvent (with aqueous solvents being preferred), and then applying the resulting composition to the carrier. If a size coat is used, it is applied on top of the color coat. To facilitate coating, the total 5 solids content of the ink is adjusted to be between 10 and 50% by weight of the ink. The coated carrier is then irradiated with laser light (e.g., as described in the commonly assigned \_\_\_\_\_ et al. application, U.S. Serial No. 08/\_\_\_\_\_, filed concurrently with this 10 application and hereby incorporated by reference) to transfer the ink from the carrier to a desired surface, e.g., the surface of a semiconductor device. Suitable lasers include CO<sub>2</sub> lasers (irradiation wavelength equals 10.6μm), Nd:YAG lasers (irradiation wavelength equals 15 1.06μm), and diode lasers (irradiation wavelength equals, e.g., 0.9μm). The particular irradiation wavelength, power, and time of application parameters are selected to ensure clean transfer.

In the case of some inks, laser irradiation both 20 transfers and cures the ink simultaneously. With other inks, a separate thermal or photochemical cure is effected following transfer. The cure conditions are selected based upon the particular prepolymers and initiators used in the formulation.

25 The invention will now be further described by way of the following examples.

Example 1

This example describes the preparation of a transfer medium having one-pass, thermally curable, 30 cationically initiated, ink.

The following ingredients were combined to form a laser-transferrable ink (all amounts in weight percent):

TiO <sub>2</sub>	55.0
Bisphenol A-DVE adduct	13.0

35201 <sup>1</sup>	24.8
PEG 3000 <sup>2</sup>	5.0
Aryl sulfonium salt <sup>3</sup>	2.0
Triton X-100 <sup>4</sup>	0.2

5 <sup>1</sup> Aqueous dispersion of bisphenol A-epichlorohydrin  
adduct formerly available from Rhone-Poulenc.

<sup>2</sup> Polyethylene glycol ( $M_n = 3000$ ) commercially available  
from Union Carbide.

10 <sup>3</sup> Aryl sulfonium salt thermal initiator of the type  
described in WO90/11303.

<sup>4</sup> Surfactant commercially available from Rohm & Haas.

Water was added to adjust the total solids content  
to 35% by weight, after which the resulting ink was  
coated onto a 1.2 mil thick polypropylene carrier film  
15 using a #15 mayer rod. The coated surface of the film  
was then placed in intimate contact with the surface of a  
molded semiconductor device. Next, a CO<sub>2</sub> laser was  
directed through the uncoated side of the carrier film to  
transfer the ink to the surface of the semiconductor  
20 device. The laser dwelled on each addressed pixel for  
16  $\mu$ sec. The power output of the laser at the point of  
contact with the coated film was 14.5 W. The device  
bearing the transferred image was then placed in a forced  
hot air oven for 30 min. at 175°C to cure the ink. After  
25 curing, the transferred image was found to be resistant  
to treatment with 1,1,1-trichloroethane (3 min. soak, 10  
brush strokes, cycled 3 times).

Example 2

This example describes the preparation of a  
30 transfer medium having a two-pass, cationically initiated  
ink in which both the color coat and the size coat are  
photochemically curable.

The following ingredients were combined to form a  
photochemically curable color coat (all amounts in weight  
35 percent):

	TiO <sub>2</sub>	55.0
	2,4-toluene diisocyanate/HBVE adduct <sup>1</sup>	35.8
	QW-16 (urethane dispersion) <sup>2</sup>	2.0
	PPZ <sup>3</sup>	5.0
5	Triton X-100 <sup>4</sup>	0.2
	UVI 6974 <sup>5</sup>	2.0

<sup>1</sup> Hydroxy butyl divinyl ether adduct.

<sup>2</sup> Pre-made urethane dispersion commercially available from K.J. Quinn.

10 <sup>3</sup> Commercially available from Idemitsu Petrochemicals Co. Ltd.

<sup>4</sup> Surfactant commercially available from Rohm & Haas.

<sup>5</sup> Triaryl sulfonium salt-based initiator commercially available from Union Carbide.

15 Water was added to adjust the total solids content to 35% by weight, after which the resulting color coat was applied to a 1.2 mil thick polypropylene carrier film using a #13 mayer rod.

20 The following ingredients were combined to form a photochemically curable size coat (all amounts in weight percent):

	EPON 1001 <sup>1</sup>	89.1
	UVI 6110 <sup>2</sup>	5.45
	FC-430 <sup>3</sup>	2.47
25	UVI 6974 <sup>4</sup>	1.68
	Perylene <sup>5</sup>	0.3
	PPZ <sup>6</sup>	1.0

<sup>1</sup> Bisphenol A diglycidyl ether commercially available from Shell Oil Co.

30 <sup>2</sup> Liquid diepoxyde commercially available from Union Carbide.

<sup>3</sup> Fluoroaliphatic polymeric ester surfactant commercially available from 3M Co.

35 <sup>4</sup> Triaryl sulfonium salt-based initiator commercially available from Union Carbide.

<sup>5</sup> Photosensitizer commercially available from Aldrich Chemical Co.

<sup>6</sup> Commercially available from Idemitsu Petrochemicals Co. Ltd.

5       Methyl ethyl ketone was added to adjust the total solids content of the size coat to 25% by weight, after which the resulting size coat was applied on top of the color coat using a #5 mayer rod.

The coated surface of the film was then placed in  
10 intimate contact with the surface of a molded semiconductor device. Next, a CO<sub>2</sub> laser was directed through the uncoated side of the carrier film to transfer the ink (color coat plus size coat) to the surface of the semiconductor device. The laser dwelled on each  
15 addressed pixel for 20  $\mu$ sec. The power output of the laser at the point of contact with the coated film was 14.5 W. The device bearing the transferred image was then cured (5 min. at a 150°C preheat, followed by a 3.6 sec exposure to UV radiation). The resulting cured  
20 printed image was found to be resistant to treatment with 1,1,1-trichloroethane (3 min. soak, 10 brush strokes, cycled 3 times).

Example 3

This example describes the preparation of a  
25 transfer medium having a two-pass, cationically curable ink in which the color coat is non-curable and the size coat is thermally curable.

The following ingredients were combined to form a non-curable color coat (all amounts in weight percent):

30	Water	54.0
	Daxad 30 <sup>1</sup>	0.5
	TiO <sub>2</sub>	38.4
	Triton X-100 <sup>2</sup>	0.5
	Shamrock 375 <sup>3</sup>	6.2
35	Rhoplex B85 <sup>4</sup>	1.4

Amsco 3011<sup>5</sup>

7.7

1 Polyacrylate dispersing agent commercially available from W.R. Grace.

2 Surfactant commercially available from Rohm & Haas.

5 3 Polyethylene wax dispersion commercially available from Diamond Shamrock.

4 Acrylic dispersion commercially available from Rohm & Haas.

5 Acrylic dispersion commercially available from Rohm & 10 Haas.

Enough ammonium hydroxide was added to adjust the pH to 8.5, after which the resulting color coat was applied to a 1.2 mil thick polypropylene carrier film at a coat weight of 69 mg/m<sup>2</sup>.

15 The following ingredients were combined to form a photochemically curable size coat (all amounts in weight percent):

	EPON 1001 <sup>1</sup>	88.2
	UVR 6110 <sup>2</sup>	11.6
20	FC-430 <sup>3</sup>	3.0
	UV 479 <sup>4</sup>	1.6
	IR 99 <sup>5</sup>	0.5
	Benzpinacole <sup>6</sup>	0.47

1 Bisphenol A diglycidyl ether commercially available 25 from Shell Oil Co.

2 Liquid diepoxyde commercially available from Union Carbide.

3 Fluoroaliphatic polymeric ester surfactant commercially available from 3M Co.

30 4 Iodonium salt thermal initiator commercially available from General Electric.

5 Dye commercially available from Glendale Protective Technologies.

35 6 Accelerator commercially available from Aldrich Chemical Co.

Methyl thyl ketone was added to adjust the total solids content of the size coat to 25% by weight, after which the resulting size coat was applied on top of the color coat using a #5 mayer rod.

5 The coated surface of the film was then placed in intimate contact with the surface of a molded semiconductor device. Next, a Nd:YAG laser was directed through the uncoated side of the carrier film to transfer the ink (color coat plus size coat) to the surface of the 10 semiconductor device. The laser dwelled on each addressed pixel for 18  $\mu$ sec. The power output of the laser at the point of contact with the coated film was 4.5 W. The device bearing the transferred image was then cured (4 min. at 175°C). The resulting cured printed 15 image was found to be resistant to treatment with 1,1,1-trichloroethane (3 min. soak, 10 brush strokes, cycled 3 times).

Example 4

This example describes the preparation of a 20 transfer medium having a one-pass, thermally curable, cationically initiated ink in which transfer and cure takes place in a single step upon laser irradiation.

The following ingredients were combined to form a laser-transferrable ink (all amounts in weight percent):

25	Talc <sup>1</sup>	30.0
	UVE 9310 <sup>2</sup>	7.0
	Copper benzoate <sup>3</sup>	0.14
	Epon 164 <sup>4</sup>	51.43
	CHVE5 <sup>4</sup>	11.43

30 <sup>1</sup> Nytal 400 commercially available from R.T. Vanderbilt.

<sup>2</sup> Photo and thermal initiator commercially available from General Electric.

<sup>3</sup> Accelerator commercially available from Aldrich Chemical Co.

35 <sup>4</sup> Epoxy novolac resin having an epoxy equivalent of 200-240 commercially available from Shell Oil.

<sup>5</sup> Cyclohexyl divinyl ether commercially available from GAF or ISI Products.

Methyl ethyl ketone was added to adjust the total solids content to 50% by weight, after which the resulting ink was coated onto a 1.2 mil thick polypropylene carrier film using a #10 mayer rod. The coated surface of the film was then placed in intimate contact with a glass slide. Next, a CO<sub>2</sub> laser was directed through the uncoated side of the carrier film to transfer the ink to the surface of the glass slide. The laser dwelled on each addressed pixel for 80  $\mu$ sec. After addressing, the transferred coating was removed from the glass slide and analyzed by differential scanning calorimetry. There was no evidence of residual heat of reaction, indicating that the transferred coating had cured during the transfer step.

Example 5

This example describes the preparation of a transfer medium having a two-pass, free radical-initiated ink in which both the color coat and the size coat are photochemically curable.

The following ingredients were combined to form a photochemically curable color coat (all amounts in weight percent):

25	TiO <sub>2</sub>	65.0
	Aquacer 355 <sup>1</sup>	11.0
	NR 440 <sup>2</sup>	18.8
	PPZ <sup>3</sup>	3.0
	Triton X-100 <sup>4</sup>	0.2
30	Daracure 4265 <sup>5</sup>	2.0

<sup>1</sup> Polyethylene wax dispersion commercially available from Diamond Shamrock.

<sup>2</sup> Acrylate-functionalized prepolymer commercially available from Zeneca Resins.

35 <sup>3</sup> Commercially available from Idemitsu Petrochemicals Co. Ltd.

<sup>4</sup> Surfactant commercially available from Rohm & Haas.

<sup>5</sup> Photochemical free radical initiator commercially available from Ciba Geigy.

Water was added to adjust the total solids content  
5 to 40% by weight, after which the resulting color coat  
was applied to a 1.2 mil thick polypropylene carrier film  
using a #13 mayer rod.

The following ingredients were combined to form a  
photochemically curable size coat (all amounts in weight  
10 percent):

NR 440 <sup>1</sup>	78.0
Ebecryl 639 <sup>2</sup>	20.0
Daracure 4265 <sup>3</sup>	2.0

<sup>1</sup> Acrylate-functionalized prepolymer commercially  
15 available from Zeneca Resins.

<sup>2</sup> Acrylate-functionalized prepolymer commercially  
available from Radcure.

<sup>3</sup> Photochemical free radical initiator commercially  
available from Ciba Geigy.

20 Water was added to adjust the total solids content  
of the size coat to 40% by weight, after which the  
resulting size coat was applied on top of the color coat  
using a #5 mayer rod.

The coated surface of the film was then placed in  
25 intimate contact with the surface of a molded  
semiconductor device. Next, a CO<sub>2</sub> laser was directed  
through the uncoated side of the carrier film to transfer  
the ink (color coat plus size coat) to the surface of the  
semiconductor device. The laser dwelled on each  
30 addressed pixel for 20  $\mu$ sec. The power output of the  
laser at the point of contact with the coated film was  
14.5 W. The device bearing the transferred image was  
then cured (5 min. at a 100°C preheat, followed by  
passage through a UV fusion oven equipped with an H bulb  
35 at a speed of 100 in./min.). The resulting cured printed

image was found to be resistant to treatment with 1,1,1-trichloroethane (3 min. soak, 10 brush strokes, cycled 3 times).

Other embodiments are within the following claims.

5       What is claimed is:

1. A transfer printing medium comprising a carrier to which is applied a curable laser-transferrable ink having one or more layers, said ink comprising  
5 (a) at least one colorant;  
(b) at least one polymerization initiator; and  
(c) at least one curable prepolymer,  
said transfer medium being capable of converting laser energy to heat.

2. The transfer printing medium of claim 1  
10 wherein said ink transfers to a surface of interest and cures in one step upon application of laser energy.

3. The transfer printing medium of claim 1  
wherein at least one of said polymerization initiators comprises a thermal polymerization initiator and at least  
15 one of said prepolymers is thermally curable.

4. The transfer printing medium of claim 1  
wherein at least one of said polymerization initiators comprises a photoinitiator and at least one of said prepolymers is photochemically curable.

20 5. The transfer printing medium of claim 1  
wherein at least one of said prepolymers comprises an epoxy-functionalized prepolymer.

6. The transfer printing medium of claim 5  
wherein said prepolymer further comprises a vinyl ether-  
25 functionalized prepolymer.

7. The transfer printing medium of claim 5  
wherein said prepolymer further comprises an acrylate-functionalized prepolymer.

8. The transfer printing medium of claim 1 wherein at least one of said prepolymers comprises an acrylate-functionalized prepolymer.

9. The transfer printing medium of claim 1  
5 wherein at least one of said prepolymers comprises a blocked isocyanate-functionalized prepolymer.

10. The transfer printing medium of claim 1  
wherein at least one of said prepolymers comprises a blend of a vinyl ether-functionalized prepolymer and a  
10 maleate- or maleimide-functionalized prepolymer.

11. The transfer printing medium of claim 1  
wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer.

15 12. The transfer printing medium of claim 1  
wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer and at least one of the layers of said ink is a non-curable color coat comprising a  
20 colorant and a thermoplastic film-forming resin.

13. The transfer printing medium of claim 1  
wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer and at least one of the layers  
25 of said ink is a curable color coat comprising a colorant, a polymerization initiator, and a curable prepolymer.

14. A laser-induced transfer printing method  
comprising the steps of

- (a) providing a transfer printing medium capable of converting laser energy to heat comprising a carrier to which is applied a curable laser-transferrable ink having one or more layers, said ink comprising
- 5        (i) at least one colorant;
- (ii) at least one polymerization initiator; and
- (iii) at least one curable prepolymer;
- (b) irradiating said medium with laser light of a predetermined wavelength to transfer said ink to a
- 10 surface of interest; and
- (c) curing said ink to adhere said ink to the surface of interest.

15. The method of claim 14 wherein the transfer and cure of said ink are effected in a single step  
15 through irradiation with said laser light.

16. The method of claim 14 wherein at least one of said polymerization initiators comprises a thermal polymerization initiator and at least one of said prepolymers is thermally curable.

20       17. The method of claim 14 wherein at least one of said polymerization initiators comprises a photoinitiator and at least one of said prepolymers is photochemically curable.

25       18. The method of claim 14 wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer.

30       19. The method of claim 14 wherein at least one of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable

prep lymer and at least one of the layers of said ink is a non-curabl color coat comprising a colorant and a thermoplastic film-forming resin.

20. The method of claim 14 wherein at least one  
5 of the layers of said ink is a curable size coat comprising a polymerization initiator and a curable prepolymer and at least one of the layers of said ink is a curable color coat comprising a colorant, a polymerization initiator, and a curable prepolymer.

10 21. The method of claim 14 wherein said the transfer and cure of said ink are effected in a single step through irradiation with said laser light.

22. The method of claim 14 wherein the transfer and cure of said ink are effected in separate steps.

15 23. A laser-induced transfer printing method comprising the steps of

(a) providing a transfer printing medium capable of converting laser energy to heat comprising a carrier to which is applied a curable laser-transferrable ink;

20 and

(b) irradiating said medium with laser light of a predetermined wavelength,

whereupon said laser light transfers said ink to a surface of interest and cures said ink to adhere said ink 25 to the surface of interest.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 94/11345A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B41M5/38

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B41M G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
4 X	PATENT ABSTRACTS OF JAPAN vol. 16, no. 36 (M-1205) 29 January 1992 & JP,A,03 244 588 (CANON K.K.) 31 October 1991 see abstract ----	1-13
9 X A	DE,A,37 15 991 (MITSUBISHI PAPER MILLS LIMITED) 19 November 1987 see column 3, line 45 - line 59; claims 1,10,11; examples 1,2 see column 4, line 50 - column 6, line 20 -----	1-13 14-23

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

12 January 1995

Date of mailing of the international search report

16.02.95

## Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040. Tx. 31 651 cno nl.

Authorized officer

A.S. Bacon